

UNDERSTANDING THE POUR POINT DEPRESSION MECHANISM-II MICROFILTRATION ANALYSIS OF CRUDE OILS

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SUMMARY

This study helps to explain the high pour point phenomena in waxy crudes and begins to explain differences in crude oils that do and do not respond to pour point depressants. Microfiltration was used to separate the waxes that precipitate out at the various temperatures in waxy crude oils. These waxes, which can be composed of saturates, aromatic, polars and asphaltenes, vary in molecular weight and composition with their temperature of precipitation in a waxy crude. Waxes that precipitate out of the crude oil solution at temperatures above the pour point are of higher molecular weight and have a high asphaltene content. The waxes that precipitate at lower temperatures have lower molecular weights and contain mostly saturates. Detailed chemical analysis showed that the temperature where asphaltenes are no longer associated with the waxes represents the maximum degree of pour point depression obtainable. This trend was verified for six waxy, high pour point crudes.

INTRODUCTION

As pointed out in the preceding paper, treating waxy crudes with pour point depressants often offers a solution to high pour point problems. However, a major uncertainty with the chemical additive treatment for reducing the pour point is that many waxy crudes only show a limited response to the pour point depressant. Additionally, the mechanism of pour point reduction, while often hypothesized, still remains unknown.

Four questions concerning pour point depression were posed in the last paper. That paper demonstrated the answers to the first three questions and indicated that the pour point is a function of the amount of saturates in the wax fraction, the waxes are composed of aromatic, polar and asphaltic components in addition to the saturates, and that the waxes in different waxy crudes can be classified into three types. Thus, when dealing with waxy crudes, the polar, aromatic and asphaltic components must be considered.

This paper attempts to answer the remaining questions posed in the last paper, and a number of questions that follow from it. Specifically, 1) What happens at the pour point temperature? 2) Why can't the pour point of many crudes be depressed beyond a certain temperature? and 3) Why are pour point depressants effective on only certain crudes?

EXPERIMENTAL

Wax Fractionation

As presented in the previous paper, a method was defined to obtain the total amount of wax in a hydrocarbon fraction at a predetermined temperature of -17.8°C (0°F). This procedure was modified to fractionate the waxes over distinct temperature ranges so that a more continuous analysis of the changing wax composition could be undertaken.

The crude was diluted (100:1) with methyl ethyl ketone and heated to 150°F . Bulk asphaltenes were removed by filtration at this temperature. The diluted sample was cooled through a series of 5.5°C (10°F) temperature intervals, with the precipitated wax being removed from the sample at each interval. The end results is a totally dewaxed oil at -17.8°C (0°F) with the waxes separated out in successive 5.5°C (10°F) temperature ranges. The separated waxes were then further analyzed by the HPLC and GPC methods discussed in the previous paper.

Centrifuge Study

Treatment with additives often does not reduce the crude's pour point to a sufficient degree. Indications are that the additive is successful with the initial range of waxes, but the either the additive is ineffective with the next range of waxes (which gives rise to the depressed pour point) or its effectiveness is inhibited by the deposition of waxes. The purpose of the centrifuge study was to separate the first precipitate of treated waxes, so that the succeeding wax fractions could be isolated for treatment and analysis. If a significant pour point reduction was obtained on this next set of waxes, the two treatments were then combined into a single treatment for the entire crude.

The basic experimental procedure was:

- 1) Treat the crude sample with the most successful additive package.
- 2) Remove the crude from the predetermined optimum oven cycle and transfer to centrifuge tubes at 22.2°C (40°F) above the treated crude's pour point.
- 3) Transfer the centrifuge tubes to a waterbath and cool the samples at 1°C/hr. (0.6°F/hr.) to 11.1°C (20°F) above the treated crude's pour point.
- 4) Preheat the centrifuge to the same temperature as in Step 3 above, and centrifuge the samples for five minutes.
- 5) Decant the top liquid phase from the settled waxes.

The top liquid phase was subjected to further treatment for pour point depression, and both the wax phase and the top liquid phase were further analyzed.

RESULTS AND DISCUSSION

This study resulted in several interesting findings which are presented below. First, an analysis of the waxes obtained at different temperatures showed that the waxes precipitating above the pour point have a high molecular weight and contain significant amounts of asphaltenes. Another finding was that a strong association exists between asphaltenes and waxes that precipitate at various temperatures. The lowest temperatures at which asphaltenes are still present with the wax appears to indicate the maximum amount of pour point reduction achievable by the use of chemical additives. Further details are offered below.

Wax-precipitation Temperature Trends

Analysis of the waxes separated at various temperatures from a crude indicates that the waxes that precipitate at temperatures above the 35°C (95°F) congealing temperature differ from those that precipitate at lower temperatures.

The first difference is shown by the GPC molecular size distribution curves (Figure 1) for Bu Attifel crude. The wax fractions isolated at 32.2°C (90°F) and 37.8°C (100°F) indicate that the waxes that precipitate below the congealing temperature is reached are composed of higher molecular weight components. Each size distribution curve represents a contribution from both higher and lower molecular weight species which show up as two distinct peaks. A reversal in the relative contributions from the two species takes place between 32.3°C and 37.8°C. At the higher temperatures (above the congealing temperature), the more sizeable contribution is from the higher molecular weight species (peak on the left), but at 32.2°C the major contribution is from the lower molecular weight components (peak on the right).

The second trend indicates that above the 35°C (95°F) congealing temperature, the wax fractions are primarily composed of asphaltenes, but at temperatures below the congealing temperature the waxes contain mostly saturates (Table I). Therefore, possible nucleating sites for wax crystal growth that precipitate at temperatures above the congealing temperature are primarily asphaltenes. These asphaltenes were initially removed by filtration during the wax separation. Apparently, some type of asphaltenes must be associated with the waxes, and they are not removed by bulk deasphalting.

TABLE I

HPLC ANALYSIS OF BU ATTIFEL WAXES SEPARATED BY MODIFIED G-281

TEMPERATURE- WAX REMOVAL	(G-281)	HPLC of the Waxes			
	WT. % WAXES	WT. % SATURATES	WT. % AROMATICS	WT. % POLARS	WT. % ASPHALTENES
100°F	1.8	4.7	0.3	---	95.0
100	1.1	24.0	0.7	0.3	75.0
95	1.0	95.5	2.1	0.4	2.0
90	0.4	95.9	2.8	0.7	0.6
80	1.7	89.7	1.7	0.2	8.4
70	1.6	89.0	2.5	0.2	8.3
60	5.6	95.9	3.5	0.1	0.4
50	2.3	94.6	4.4	0.6	0.4
40	2.4	96.6	3.0	0.4	---
30	3.6	97.2	2.7	0.1	---
20	4.1	95.7	3.6	0.7	---
0	5.0	96.8	2.7	0.5	---
-20	4.3	96.3	3.2	0.5	---

Aside from the uncertainty as to the source of the asphaltenes, it is understandable why the higher temperature waxes are composed of asphaltenes. Asphaltenes are high molecular weight species and can be viewed as being more peptized (less flocculated) at the higher temperatures. Therefore, asphaltenes would tend to associate with the higher temperature waxes. The presence of these asphaltenes with the higher temperature waxes could also explain why the GPC molecular size distribution contains two peaks. The peak on the left probably represents the asphaltenes, while the peak on the right might represent the saturates and associated polars and aromatics.

This reasoning does not, however, explain either how or why the asphaltenes are associated with any of these waxes, since a bulk deasphalting step should have removed them. Further analysis of this asphaltene association yielded some interesting results which are outlined below.

Asphaltene Effect

As noted, asphaltenes are associated with the waxes, even though they should have been removed by a bulk deasphalting step during the wax separation. This association was verified by determining the saturates, aromatics, polar, and asphaltene content of Bu Attifel in two different manners.

First, Bu Attifel crude was directly separated by group type into saturates, polars, aromatics, and asphaltenes and volatiles by HPLC. Conversely, by total wax separation at 0°F, the crude was separated into the total wax, oil and bulk asphaltene fractions. These fractions were then analyzed by HPLC to yield the group types contained in the fractions. The same total amounts of the saturates, aromatics, polars and asphaltenes should be obtained for both separation methods.

As can be seen in Table II, this does not appear to be true for the asphaltenes and saturates. Only when the saturates and asphaltenes are added together is conservation of mass satisfied. Apparently, the saturates and asphaltenes are associated with one another and do not totally separate from one another during the bulk deasphalting step. Asphaltenes have been reported to be associated with polar and aromatic components during deasphalting, but in this case, the deasphalting step is leaving asphaltenes behind.

TABLE II

BU ATTIFEL CRUDE COMPONENT ANALYSIS

HPLC Analysis After Separation Into Wax,
Asphaltenes, and Oil By Gulf Method 281

Components	Wt. %	Saturates	Insolubles (asphaltenes)	Polars	Aromatics	Volatiles
Wax	29.5	= 27.317	+ 1.475	+ .059	+ .649	+ 0
Asphaltenes	3.9	= .17	+ 3.72	+ 0	+ 0	+ 0
Oil	41.0	= 36.018	+ 0	+ .241	+ 4.751	+ 0
Volatiles	25.6	= 0	+ 0	+ 0	+ 0	+ 25.6

Total	100.00	= 63.505	+ 5.195	+ .3	+ 6.40	+ 25.6
		68.7				

HPLC Analysis of the Total Crude

Total Crude	100.00	= 67.8	+ 0.9	+ .31	+ 5.79	+ 25.6
		68.7				

It is interesting to note the precipitation temperature at which the waxes no longer contain asphaltenes (Table I). No asphaltenes are found with the waxes that precipitate at temperatures below 10°C (50°F). It should be noted that Bu Attifel crude's pour point has never been depressed below this temperature.

Similar analysis of Cabinda Crude (Table III) verifies the Bu Attifel results. As with Bu Attifel crude, asphaltenes are associated with the saturates at higher precipitation temperatures. Asphaltenes are, however, found with all of the waxes that precipitate out to -17°C (0°F). This is especially interesting since this wax precipitation temperature also represents the maximum depressed pour point obtained for Cabinda crude by using chemical additives.

TABLE III

HPLC ANALYSIS OF CABINDA WAXES SEPARATED BY MODIFIED G-281

TEMPERATURE- WAX REMOVAL (°F)	(G-281)	HPLC of the Waxes			
	WT. % WAXES	WT. % SATURATES	WT. % AROMATICS	WT. % POLARS	WT. % ASPHALTENES
100	2.1	12.4	4.1	8.3	75.2
90	0.3	20.4	7.2	28.8	43.6
80	3.1	57.0	13.6	24.4	1.7
70	2.0	70.5	11.6	17.5	0.4
60	1.4	70.3	12.2	17.4	0.1
50	2.2	70.3	12.7	16.6	0.4
40	3.7	60.0	16.4	23.3	0.3
20	4.4	66.7	16.3	16.9	0.1
0	3.3	66.2	18.5	15.1	0.2

Additional analysis of six crude oils confirms that asphaltenes are associated with the level of pour point depression. Table IV summarizes the maximum effect of pour point depressants on the crudes. Note that this temperature also represents the temperature at which the asphaltene-saturate association ends.

TABLE IV

ASPHALTENE - POUR POINT DEPRESSION TREND

CRUDE	WASATCH	GREEN RIVER	HANDIL	GOBBS
Pour Point (°F)	105	95	90	85
Maximum Depressed Pour Point (°F)	105	60	70	30

Temperature-
Wax Removal

HPLC Indication of Asphaltene

110	*	*	*	*
100		*	*	*
95		*	*	*
90		*	*	*
80		*	*	*
70		*	*	*
60		*		*
50				*
40				*
30				*
20				
0				

*Denotes presence of asphaltenes.

The treated and untreated waxes in Bu Attifel crude were isolated by the centrifuge method and analyzed with HPLC. This study indicated (Table V) that the untreated portion of Bu Attifel crude contained no asphaltenes.

TABLE V

ANALYSIS OF UNTREATED, CENTRIFUGED BU ATTIFEL WAXES

(G-281)		HPLC OF THE WAXES				
TEMPERATURE- WAX REMOVAL (F°)	WT. % WAXES	WT. % SATURATES	WT. % AROMATICS	WT. % POLARS	WT. % VOLATILES	WT. % ASPHALTENES
0	33.9	70.9	6.5	0.4	22.2	0.0

Based on these results it appears that the presence of asphaltenes with waxes indicates that the waxes will be susceptible to wax crystal modification and subsequent pour point reduction induced by chemical additives. It is apparent that the asphaltenes are either a symptom of a wax crystalline form that is susceptible to modification, or themselves caused a weak link in the wax crystal and thus cause the wax to be susceptible to modification.

Past research has suggested that asphaltenes can aid or act as wax crystal modifiers (pour point depressants), but it was never possible to predict their effect on a given crude or distillate. Therefore, these results also begin to explain some of the ambiguities encountered with using asphaltenes as pour point depressants. Plain bulk asphaltenes may never be associated with or interfere with a given wax structure, but specific asphaltenes, such as those associated with the waxes in Cabinda crude may be necessary.

CONCLUSIONS

- 1) Waxes that precipitate at temperatures above the congealing temperature contain mainly asphaltenes. These waxes also are composed of higher molecular weight species than the waxes that precipitate at temperatures below the congealing temperature.
- 2) Asphaltenes appear to play an important role in pour point reduction. They either symptomize waxes that are susceptible to chemical additives, or else interfere with the congealing mechanism. The presence of asphaltenes with waxes indicates that the waxes will be modified by chemical additives.
- 3) Different high pour crudes have different wax precipitation temperature limits of the wax-asphaltene association. Therefore, the maximum pour point depression attainable with each crude appears to be a function of the precipitation temperature where asphaltenes are no longer associated with the waxes.

- 4) The bulk asphaltenes may be chemically different from the asphaltenes found associated with the Bu Attifel and Cabinda waxes.

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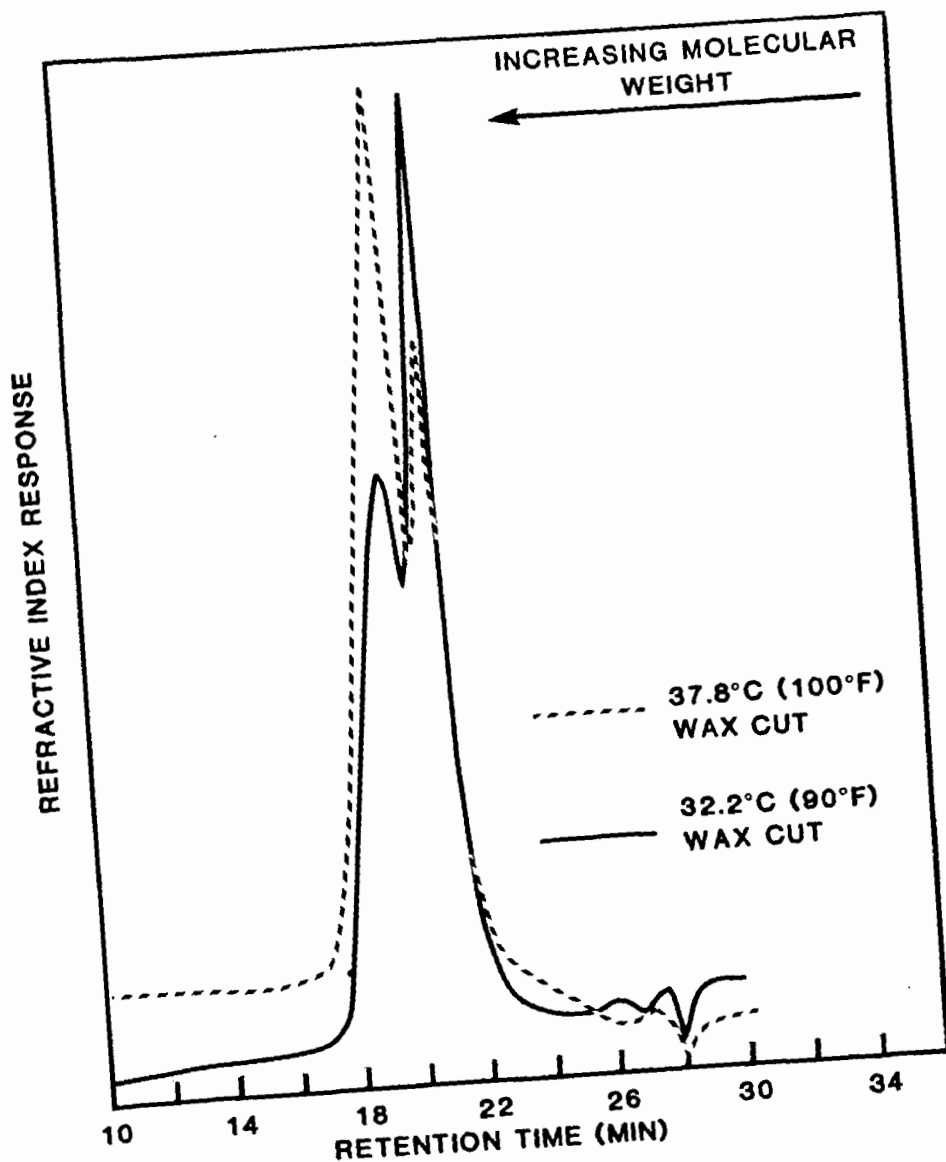


Fig.1 MOLECULAR WEIGHT DISTRIBUTION TREND
CHANGE BETWEEN BUATTIFEL WAX FRACTIONS